# REPORTED DISPOSAL OF 2,4,5-T ON OTTAWA NATIONAL WILDLIFE REFUGE

By: William Kurey
U. S. Fish and Wildlife Service
Reynoldsburg, Ohio

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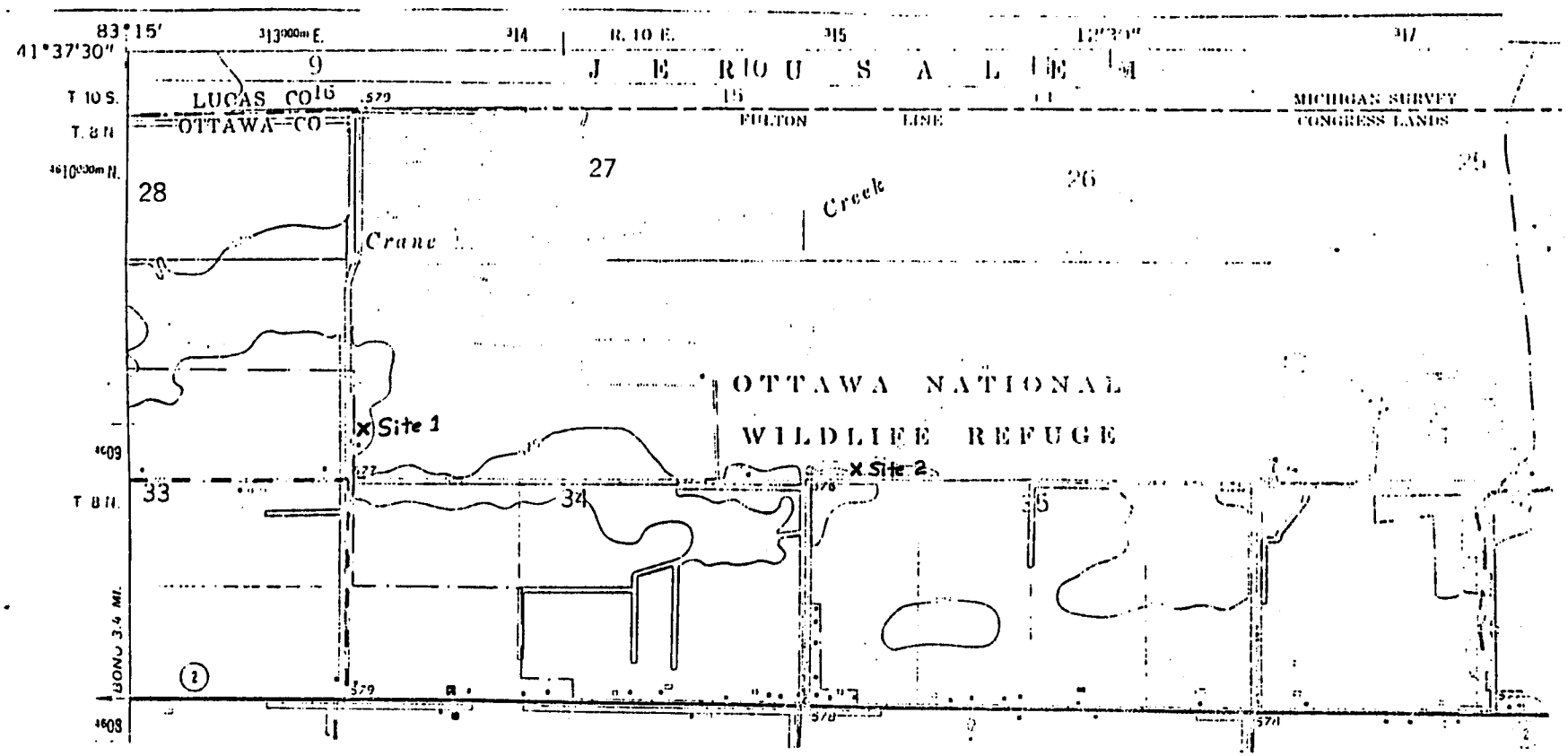
## SITE BACKGROUND

The Ottawa National Wildlife Refuge (ONWR) is located on the shore of Lake Erie near Oak Harbor, Ottawa County, Ohio. Early in 1986, ex-employees of the ONWR reported having buried one full and one partially full 55 gallon drums on the refuge. The ex-employees, Nelson Dornbusch (419-898-1166) and Woody Hollbrook (419-635-2544), remembered having disposed of the drums in about 1973 at one of two possible locations, the exact details not being remembered. Because they had a backhoe, the drums could be buried as deep as 10 feet. The material in the drums was a herbicide used to control brush; it came in olive drab drums marked DOW and could have been military surplus. There is probably about 80 gallons of herbicide in the burial. Precise locations of the suspected burial sites are located on the attached map (R.10 E., T.8N., Sections 34 and 35 - Oak Harbor quadrangle). The two sites are about 1 mile apart.

## SITE GEOLOGY

The ONWR is underlain by Monroe Limestone of Silurian or Devonian age (Bownocker, J.A. 1981. Geologic Map of Ohio). The thickness of the overlying glacial deposits averages about 25 ft. in Ottawa County (Davis Besse Supporting Information). However, the Ottawa County Soil survey gives the depth to bedrock as greater than 60 ft. Well logs in the area of the sites show a depth to bedrock of 56 to 60 feet.

The confined aquifer (bedrock) in the area of the sites flows westward from the lake and may be connected to the lake. Well water levels (here regarded as a plane surface) ranged from 5.60 to 6.35 feet below ground level in the three wells tested. The well levels reflect pressure from the bedrock aquifer, not




Location Map, Oak Harbor Quadrangle, Ohio. Scale 1:24,000

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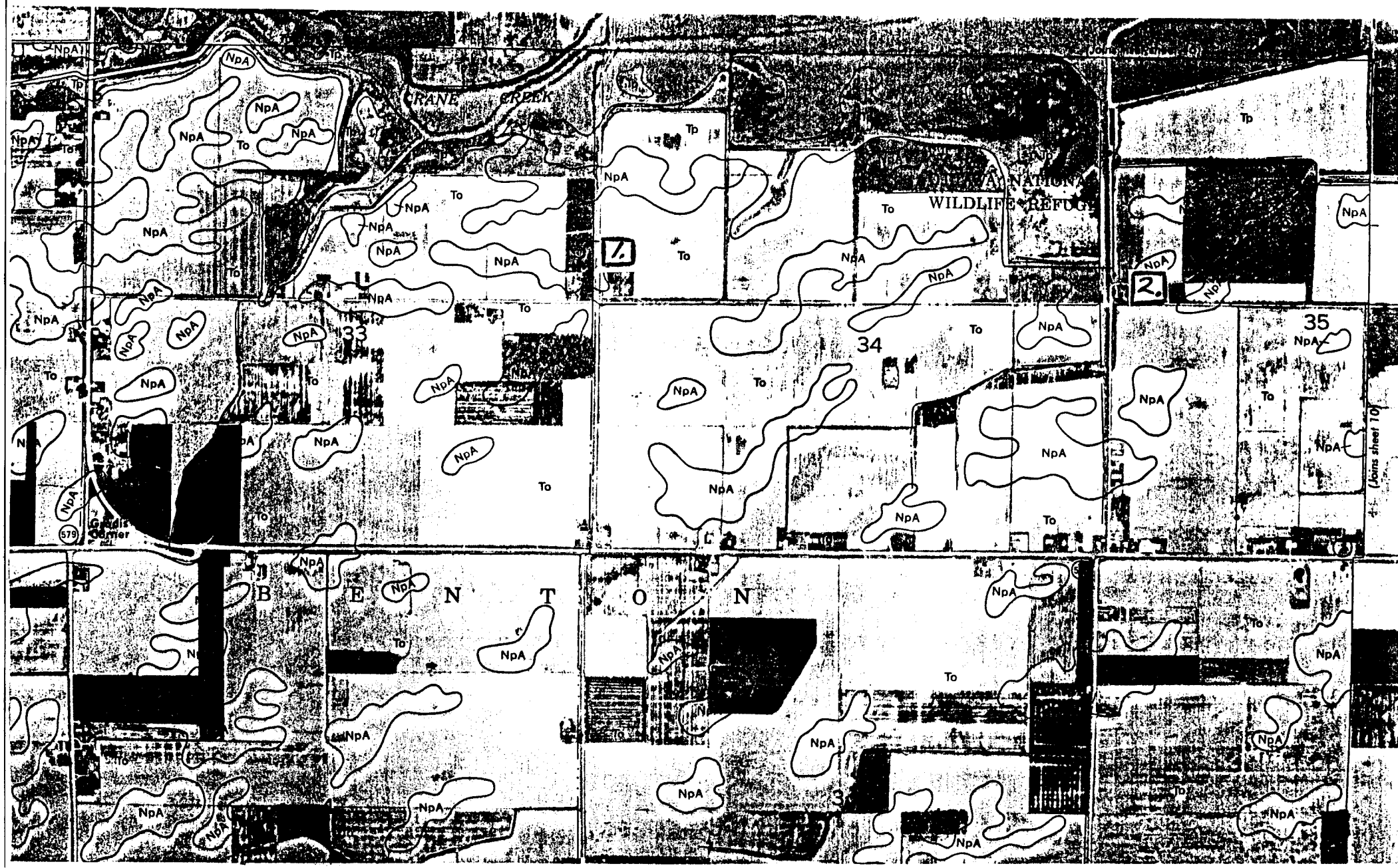

water in the overlying clays (assuming the well cases are tight). This aquifer would normally have no connection with the overlying clay soils.

The two suspected burial sites are in the Toledo-Nappanee association soils. These are deep, nearly level, poorly drained soils formed in clayey glacial lake bed sediments and glacial till. Surface soil at suspected burial location 1 (Refuge Manager's house) is either Toledo silty clay (To) or Nappanee silty clay loam (NpA). Location 2 is most probably on Toledo silty clay (To) (USDA. 1985 Soil Survey of Ottawa County). The To soil contains 3-6% organic matter, the NpA 1-3% organic matter, and both have permeabilities of from .06 to .6 inches/hour. To and NpA soils are both highly corrosive to steel - which could mean any drums are not intact.

Mr. Kevin Brean of the U. S. Geological Survey suggested that the site area could be geologically similar to the Evergreen Landfill in Northwood, Ohio (Toledo area) to the west of ONWR. The vertical permeability of cores at the Evergreen Landfill ranged from $1 \times 10^{-8}$ to $5 \times 10^{-8}$ cm/sec ($1.42 \times 10^{-5}$ in/hr and $7.09 \times 10^{-5}$ in/hr) and the only significant lateral movement was through sand and gravel lenses and fractures. He further suggested there were probably few fractures at the ONWR sites because the area had not been disturbed much. However, the contact between Nappanee and Toledo soils in the vicinity of Site No. 1 could be an area of fractures.

Groundwater leachate plumes tend to remain intact with slight dispersion and diffusion mainly along the edges. The depth of a plume usually increases with distance from the source. The direction of groundwater flow is generally from higher topographic areas to surface water discharge areas but site geological characteristics such as impermeable layers and heavily pumped wells can greatly alter flow direction.

With the above generalities in mind, the topographic map suggests that any ground water flow in the soil at location 1 would be towards the east or northeast. At location 2, the expected directions would be towards north and east. Assuming a 2 ft head over 300 ft and permeabilities of from .06 to .6 inches/hour from the soil survey, Darcy's law gives the following groundwater velocities:

$$V = K \frac{h1-h2}{L} = 0.60 \text{ in./hr.} \times \frac{2 \text{ ft}}{300 \text{ ft}} = .0042 \text{ in./hr.}$$

$$= 0.06 \text{ in./hr.} \times \frac{2 \text{ ft}}{300 \text{ ft}} = .00042 \text{ in./hr.}$$

Over a period of 17 years (the approximate age of the drum burial) the ground water flowing through the burial could have traveled 5.2 to 52.1 ft.

Using another form of Darcy's law, the volumes of water that could have passed through the maximum cross sectional area of the 2 drums are:

$Q = AV$ = (1564 sq. in.) (.0042 in./hr.) = 6.57 cu. in./hr.
= 33.3 cu. ft. per year

$Q = AV$ = (1564 sq. in.) (.00042 in./hr.) = 0.66 cu. in./hr.
= 3.33 cu. ft. per year

The above figures are very conservative because they presume more head pressure than likely, the drums would have remained intact for some number of years, and permeability would likely be around .06 in./hr., probably much less.

Due to the virtually impermeable nature of the clay soils, we expect that any 2,4,5-T that has entered the environment is still close to the burial, probably within 5 ft. and that the volume of earth and water contaminated does not exceed 50 cu. ft.

## NATURE AND EXTENT OF THE PROBLEM

The herbicide 2,4,5-T (2,4,5-trichlorophenoxyacetic acid) was developed in the 1940s and registered as a pesticide in 1948. In about 1969, 2,4,5-T became controversial because it contains dioxin (specifically 2,3,7,8-tetrachlorodibenzo-p-dioxin or 2,3,7,8-TCDD) formed during the production process. There are 75 dioxin isomers of which 2,3,7,8-TCDD is considered the most toxic. Some of the other isomers are believed to be relatively innocuous. In some test animals 2,3,7,8-TCDD is one of the most toxic substances known, but apparently not in humans. In humans, the hallmark of exposure to dioxins is

chloracne, usually more severe than adolescent acne. Other symptoms of exposure include altered liver and lipid metabolism, porphyria, neurotoxicity, changes in the blood, and hyperpigmentation. There is still some question if 2,3,7,8-TCDD is a carcinogen.

2,4,5-T is relatively soluble in water and has a low octanol-water partitioning coefficient of 0.533 at pH 7 while butyl esters of 2,4,5-T have a high partitioning coefficient number of 64,000. High partitioning coefficients are related to high sorption. Hydrolysis in water of 2,4,5-T esters occurs rapidly (depending on pH), reducing the toxicity of the ester form to more like that of other forms of 2,4,5-T. Hydrolysis also decreases the ability of the 2,4,5-T ester to bind to sediments. The density of 2,4,5-T is about 1.8 that of water.

According to Lutz, et al. (1973), 2,4,5-T applied to the surface could move through agricultural soil to groundwater only through large pores or cracks. The higher the organic content of the soil the less movement there will be. Norris (1981) also noted little or no leaching of 2,4,5-T in rangeland despite 13 to 45 cm of precipitation within 12 weeks of the application.

2,4,5-T and most of its amine salts and some of its esters are quite low in toxicity and have a wide margin of safety to fish when applied according to the label (Kenaga, 1974). Some of the esters are more toxic than other forms of 2,4,5-T.

Probably as a result of its TCDD content, 2,4,5-T is an irritant and can cause contact dermatitis in man (Casarett and Doull, 1980). The NIOSH guide recommends respiratory protection begin at 50 $mg/m^3$ of 2,4,5-T; the permissible exposure limit is 10 $mg/m^3$; and the IDLH (immediate danger to life and health) level is 5000 $mg/m^3$. As an example of expected levels under relatively high atmospheric concentration conditions, the amount of 2,4,5-T in the air from weed control spray operations ranges from less than 0.004 ug/l (4 $ug/m^3$) to 0.169 ug/l (169 $ug/m^3$) the mean being 0.02 ug/l (20 $ug/m^3$) (Norris, 1981).

With 2,4,5-T esters, vapor production slows or ceases as ester hydrolysis occurs. The atmospheric concentration of 2,4,5-T at the ONWR sites is not likely to come near any of the NIOSH limits, or even levels encountered from

spray operations. In fact the vapor pressure of TCDD, the major hazard, is $4.0 \times 10^{-7}$ mm Hg at 30.1°C. For comparison, the vapor pressure of water at 30°C is 31.82 mm Hg. For a diffusion path of 1 cm in air at saturation concentration, the diffusion flux for TCDD is $1 \times 10^{-15}$ g/cm$^2$ second (Freeman et al., 1985). Because excavations at the ONWR sites were outside (well ventilated), any 2,4,5-T encountered would probably have been bound to solids, and the fact that vapors could not be expected to reach levels of concern, respiratory protection was not necessary in the excavation operation.

TCDD is very persistent where it is protected from light. The half life may be 3 to 10 or more years in soil. Dioxin binds to organic surfaces, including plant roots, and in the bound form is unavailable for absorption and translocation. TCDD can translocate in plants but uptake is generally very small with extremely small accumulation in fruits and seeds. There is no evidence that plants are physiologically affected by dioxin contamination.

Some formulations of 2,4,5-T contained up to 33 ppm of TCDD (Mullison, 1980). Production grade 2,4,5-T contained 0.03 ppm in 1981. The amount of TCDD in military phenoxy herbicide ranged from 65.6 ppm to 1.98 ppm (Young, et al., 1983). Eisler (1986) cites Hardell (1983) as giving the amount of TCDD in various 2,4,5-T ester formulations as ranging from 0.22 to 0.95 ppm. The amount of TCDD at the ONWR site could be expected to fall within this range because it was an ester formulation. If we assume that 80 gallons of 2,4,5-T ester was buried in two drums at the site, then the total amount of TCDD buried would have been about 288 mg (based on the 0.95 ppm (mg/l) maximum in 2,4,5-T ester). Using 288 mg as the original amount of buried TCDD and 10 yrs as the half life in soil, after 17 years there should be about 51 mg of TCDD in any burial. If 50 mg of TCDD in a burial was evenly distributed in 50 cubic feet of soil (density 1.6 g/cm$^3$) the concentration would be about 1 ug/kg(1ppb).

TCDD is almost insoluble in water and could be expected to remain on soil surfaces (Norris, 1981). Norris (1981), cites Kearney, et al. (1973) as concluding that because it is immobile in soils, TCDD would be "no groundwater contamination problem." Norris also cites Yockim, et al. (1978) as finding that TCDD equilibrated between sediment and water phases in about 1 day with 3 ng/l in water and 0.1 mg/kg of TCDD in sediment (a ratio of 33,000:1). The longer the time TCDD is bound to soil, the harder it becomes to extract.

TCDD is extremely toxic to animals. LD50s in mammals range from 0.6 to 1157 mg/kg body weight in mammals and from 810 ug/kg to 15 mg/kg body weight in birds. However, unlike aquatic animals, terrestrial animals do not concentrate TCDD to a considerable extent.

The only potential health risks involved with this suspected burial would be from Site No. 1 through well contamination at the Refuge Manager's house. The 2,4,5-T ester and any dioxin it may contain would be well sequestered by the clay soils in which the drums might be buried. The well at the Refuge Manager's house is over 100 feet from the suspected burial site and extends into bedrock.

Because of the close proximity of the suspected burial locations to the Refuge Manager's house, well water in 2 locations was tested and no 2,4,5-T was found at a detection level of 1 ug/l. The addresses of the wells tested were:

Mike Tansy (Refuge Manager)
6585 N. Stange Road
Graytown, OH 43432

Robert Reynolds
16047 Kreuse Road
Graytown, OH 43432

The existence of the buried drums is still unproven. Any metal drums containing the liquid 2,4,5-T ester could have disintegrated by now making discovery of the burial virtually impossible if it was not at one of the two suspected sites. On November 18, 1986, U.S. EPA's Technical Assistance Team (TAT) conducted a survey of the ONWR sites using electromagnetic induction and ground penetrating radar equipment. One target was found at Site 1 which could be a drum, and at Site 2 metal was detected but there was no certainty that either of these readings were really drums. The positions were staked for future excavation.

SITE SURVEY AND EXCAVATION

On November 18, 1986 at our request, Mr. Jim Ursic and Mark Vendl of the U.S. EPA, Region 5, conducted a ground penetrating radar survey and electromagnetic induction survey at two locations within the refuge where the drums were suspected of being buried (see Appendix). Survey flags were used to mark

locations where readings indicated the possibility of buried drums. Compass bearings and distances were determined between the survey flags and in relation to the well at the Refuge Manager's residence in the event that the flags were missing when we returned to excavate.

On September 21, 1987 excavation began with a backhoe at the southern most flag of site 1. The 6-foot deep trench turned out to be right at, and parallel to, the southern wall of the old pit. The south side of the trench was undisturbed clay and the north side contained debris and organic matter. The clays were light colored grays and browns streaked with dark red/brown iron. At about 3 ft. depth water started to flow into the trench from the north wall. Evidently the debris and loose soil of the old pit has allowed rain water from the surface to collect in the numerous voids. The old pit acted as a reservoir because of the impermeable clay in which it way dug. The surrounding clay did not appear to contain much moisture. Undisturbed clay marking the bottom of the old disposal pit was encountered at a depth of about 6 ft.

According to the EPA survey report this first trench was the only one likely to contain a drum. This did not turn out to be the case. The other trenches did turn up metal (old cable and crushed sheet metal) but nothing that could be identified as having been a drum. The metal did not appear to have been heavily corroded and this may have been because the highly organic conditions in the old pit were so different from the surrounding clay.

Two trenches were excavated and sampled at site 1 on September 21, 1987 and two on September 22, 1987. Trench 3 was in undisturbed ground and was excavated only 2-3 ft. deep. The survey of site two had produced only one point where it looked like there was metal or a drum might be buried. Excavation of the flagged point and three other unmarked points in the area showed the entire area to be undisturbed ground. There was an old disposal pit at site 2 but this could not have contained the drums because it was begun and finished in 1984 long after Dornbusch and Hollbrook had left the Service.

Samples of sediments were taken at various depths at site 1 as well as samples of the ground water contained in the old pit. No samples were collected from site 2 because the ground was undisturbed. All trenches were refilled immediately after samples were collected.

## ANALYSIS

In March, 1986 Mr. Dornbusch supplied us with an old sample of the herbicide that he thought was buried. He said he had taken some of the material home before the rest was buried. The sample of material given to us by Mr. Dornbusch was sent to Mississippi State University for analysis in late March, 1986. Analysis of the sample by high performance liquid chromatography indicated that the sample contained 18.75% 2,4,5-T and this identity was confirmed by infrared spectroscopy. The solubility characteristics of the sample in water indicated it was an ester form of 2,4,5-T.

Numerous soil samples and some water samples were taken at various depths from the trenches excavated at site 1 in September 1987. Soil samples were collected with stainless steel spoons, cleaned in acetone between samples. The sample containers were cleaned 500 ml widemouth jars from the I-Chem Co. Samples were frozen upon return to the Reynoldsburg FWS office on September 22, 1987.

Seven sediment samples were submitted to Mississippi State University on September 6, 1988 for chlorophenoxy acid herbicides analysis. Owing to delays caused mainly by Patuxent Analytical Control Facility (PACF), results of the analyses were not available until March 5, 1990, despite the promised 90-day turn-around period. Results of the GC/MS analyses were negative for all samples at a level of detection of 0.01 ppm.

## SUMMARY

Surveys and chemical analyses of samples from the suspected sites of 2,4,5-T burial on ONWR failed to prove there had ever been such a disposal. If such a burial did occur we will not be able to find it without better directions to the burial site. Further, the heavy clay soils of the area make it highly unlikely that any buried 2,4,5-T would enter an aquifer or become available to the surface environment. Horizontal movement of any buried 2,4,5-T would likely not occur and downward vertical movement would be minimal or not occur. We do not recommend further search for a burial site.

Soil Analysis for Chlorophenoxy Acid Herbicides (2,4,5-T) from Excavations near the Refuge Manager's House at Ottawa National Wildlife Refuge

| Sample No. | Hole No. | Depth (ft) | Matrix | Weight(g) | Moisture % | Residue |
|---|---|---|---|---|---|---|
| 1 | 1 | 3 | Soil | 458 | 28.2 | ND |
| 2 | 1 | 3 | Soil | 336 | 21.4 | ND |
| 4 | 1 | 6 | Soil | 426 | 21.8 | ND |
| 5 | 2 | 2.5 | Soil | 456 | 27.6 | ND |
| 8 | 2 | 6 | Soil | 395 | 10.6 | ND |
| 9 | 2 | 5 | Soil | 364 | 21.2 | ND |
| 11 | 4 | 1.5 | Soil | 252 | 12.8 | ND |

Note: ND = Not Detected
Level of Detection = 0.01 ppm

History of Response Actions:

3/7/86 Field trip to ONWR to interview Nelson Dornbusch and get a sample of material that was buried

4/18/86 Received laboratory analysis results of suspected buried material

5/13/86 Received test results of water quality in refuge well

6/6/86 Service letter officially requesting assistance from U.S. EPA Technical Assistance Team (TAT) in conducting a search for the buried drums

8/4/86 Letter to Kate Wilson of Ohio EPA outlining our knowledge of the suspected burial

9/16/86 Field trip to ONWR to meet Kevin Brean of USGS and look at wells and geology

11/18/86 U.S. EPA TAT Team conducted etectromagnetic induction and ground penetrating radar survey of suspected sites

12/30/86 Received U.S. EPA report on electromagnetic induction and ground penetrating radar surveys

9/21/87 Excavation of suspected burial sites

10/23/87 Field office submitted catalog of samples to Region 3 FWS

2/16/88 Region 3 submitted sample catalog to PACF

7/27/88 Region 3 resubmitted sample catalog to PACF after discussion

8/8/88 Received approval of request for nonroutine analysis

9/1/88 Received approval to submit samples

9/6/88 Submitted samples from excavation for analysis

- PACF DELAYS -

3/5/90 Received results of analysis samples from suspected burial site

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